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(54) Solid electrolyte type fuel cell and method for producing the same

Brennstoffzelle mit festem Elektrolyten und Verfahren zur Herstellung derselben

Pile à combustible à base d'un électrolyte solide et méthode pour sa production

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obtain a zirconia film of a thickness of about 100 μm. Then, the thus obtained layered structure was heat treated in air at 1,000°C, 1,200°C, 1,300°C, 1,400°C or 1,500°C for 3 hrs to densify the zirconia film 26. Thereafter, N_2 gas permeation coefficients of the zirconia film after the heat treatment were measured. The measur d results are shown in Fig. 20.

When compared the specimens of Examples 4 and 5 with the specimens of Examples 6 and Comparative Example 3, N_2 gas permeation coefficients of the specimens of Examples 4 and 5 heat treated at 1,400°C are on the order of 10^{-10}, whereas those of Example 6 are on the order of 10^{-9} and those of Comparative Example 3 are on the order of 10^{-6}. Thus, it is considered that the sintering of the zirconia film 26 is accelerated in Examples 4 and 5 by virtue of the manganese compound films 25 and 27. Also, the bending strength of the specimens of Examples 4 and 5 are 4 times or more higher than those of Example 6.

The specimen of Example 4 was analyzed in the following way by a photograph taken by a microscope. The specimen was that heat treated in air at 1,400°C for 3 hrs. The specimen was polished at a cross-section thereof and the polished cross-section was observed by a SEM. A photograph taken by the SEM is shown in Fig. 21. From the photograph, it can be seen that the airtight zirconia film 26A has a microstructure uniformly densified from the interface of the air electrode substrate to nearly the surface.

The specimen of Example 6 was also analyzed in the above way. The specimen was that heat treated in air at 1,400°C for 3 hrs. A photograph taken by the SEM is shown in Fig. 22. From the photograph, it can be seen that the airtight zirconia film has a microstructure not densified near the surface though it was densified at the interface between the air electrode substrate.

From these experimental results it is understood that the whole solid electrolyte film can be uniformly densified by the adoption of the structure of the present invention, so that the airtight property of the solid electrolyte film can be improved to increase the SOFC output and the fuel utilization efficiency. Also, the strength of the solid electrolyte film can be remarkably increased by the densification, so that a reliable SOFC can be mass produced.

In order to prove these points in practice, a past of nickel-zirconia cermet (Ni:8YSZ=6:4 in volume ratio) was screen printed to a round shape of a diameter of 6 mm on a surface of the specimen of Example 4 (heat treated in air at 1,400°C for 3 hrs), and baked in air at 1,350°C for 2 hrs.

A specimen of the thus produced flat plate-shaped SOFC was fixed on a jig, hydrogen humidized at room temperature was introduced into the fuel electrode film side of the SOFC, while an oxygen gas was introduced into the air electrode substrate side of the SOFC to generate an electric current at 1,000°C. A current-voltage characteristic graph of the generated electric current was measured, and the results are shown in Fig. 23.

In the same manner as described above, a fuel electrode film was provided on a surface of the sample of Example 6 (heat treated in air at 1,400°C for 3 hrs) to prepare a specimen of a flat plate-shaped SOFC, and a current-voltage characteristic graph thereof was measured in the same manner as described above, and the same results as shown in Fig. 14 were obtained.

Also, in the same manner as described above, a fuel electrode film was provided on a surface of the sample of Comparative Example 3 (heat treated in air at 1,550°C for 3 hrs) to prepare a specimen of a flat plate-shaped SOFC, and a current-voltage characteristic graph thereof was measured in the same manner as described above, and the same results as shown in Fig. 15 were obtained.

As a result, open end voltage of the sample of Example 4 was 1,120 mV, while those of Example 6 and Comparative Example 3 were 1,070 mV. In the sample of Example 4, the open end voltage was increased, the short-circuiting current was increased, and the output of the unit cell was improved.

Although the present invention has been explained with specific examples and numeral values, it is of course apparent to those skilled in the art that various changes and modifications thereof are possible without departing from the broad aspect of the present invention as defined in the appended claims.

Claims

1. A solid electrolyte type fuel cell including an air electrode substrate (1) made of a perovskite series complexed oxide having a composition of the formula $(La_{1-y}A_y)MO_3$ wherein A is at least one alkaline earth metal, M is manganese or cobalt, and y is $O \leqq y \leqq 0.4$, a zirconia solid electrolyte film (2) containing manganese or cobalt solid soluted at at least the neighborhood of the interface thereof with the air electrode substrate, and a fuel electrode film (3) formed on the solid electrolyte film at a surface opposite to the air electrode substrate, wherein the fuel cell is substantially not provided with a highly resistive layer made of a compound containing lanthanum and zirconium at the interface between the air electrode substrate and the solid electrolyte film.

2. The solid electrolyte type fuel cell of claim 1, wherein the air electrode substrate (1) is a structural body having a thickness of at least 0.5 mm.

3. The solid electrolyte type fuel cell of claim 1 or 2, wherein the air electrode substrate (1) is a porous body having a porosity of at least 25%.

4. The solid electrolyte type fuel cell of any one of claims 1 to 3, wherein the zirconia solid electrolyte film (2) has a manganese or cobalt solid soluted therein in an amount of 3-15 mole%.

5. A method for producing a solid electrolyte type fuel cell, comprising forming an intermediate layer (25) consisting of manganese or a manganese compound or cobalt or a cobalt compound on a surface of a material for an air electrode (24) made of a perovskite series complexed oxide having a composition of the formula $(La_{1-y}A_y)MO_3$ wherein A is at least one alkaline earth metal, M is manganese or cobalt, and y is $0 \leqq y \leqq 0.4$, providing on the surface of the intermediate layer a film (26) made of a material for forming on heat treatment a zirconia solid electrolyte to form a layered structure, and heat treating the thus obtained layered structure to extinguish the intermediate layer (25) while changing the film (26) of the material for the solid electrolyte into an airtight zirconia solid electrolyte film.

6. The method of claim 5, wherein said intermediate layer (25) is formed by plasma thermal spraying on the surface of the raw material for the air electrode.

7. The method of claim 5, wherein the intermediate layer (25) is formed by forming a coating containing manganese or a manganese compound or cobalt or a cobalt compound on the surface of the raw material for the air electrode, and then heat treating the coating.

8. The method of claim 5, 6 or 7, wherein the film (26) of the material for forming the zirconia solid electrolyte is formed by plasma thermal spraying.

9. A method for producing a solid electrolyte type fuel cell including the steps of providing, on an electrode of the cell, a film (26) of a material for forming on heat treatment a zirconia solid electrolyte, the electrode (24) being an air or fuel electrode made of a perovskite series complexed oxide having a composition of the formula:

$$(La_{1-y}A_y)MO_3$$

wherein A is at least one element selected from alkaline earth elements, M is manganese or cobalt, and y is $0 \leq y \leq 0.4$, providing a compound film (27) made of manganese or a manganese compound or cobalt or a cobalt compound on the surface of the film (26) of material for the solid electrolyte to form a layered structure, and then heat treating the layered structure to change the film (26) of the material for the solid electrolyte to an airtight zirconia solid electrolyte film.

10. The method of claim 9, wherein an intermediate film (25) made of manganese or a manganese compound or cobalt or a cobalt compound is provided on the surface of the electrode (24) and the film (26) of the material for forming the zirconia solid electrolyte is provided on the surface of the intermediate film (25).

11. The method of claim 9 or 10, wherein the film (26) of the material for forming zirconia solid electrolyte is formed by plasma thermal spraying.

12. The method of claim 9, 10 or 11, wherein the compound film (27) is formed by plasma thermal spraying.

13. The method of claim 9, 10 or 11, wherein the compound film (27) is formed by a wet process.

14. The method of claim 13, wherein the wet process is tape casting, slip casting or extrusion.

Patentansprüche

1. Brennstoffzelle mit Festelektrolyt, umfassend ein Luftelektrodensubstrat (1) aus einem komplexierten Oxid aus der Perovskitreihe mit einer Zusammensetzung der Formel $(La_{1-y}A_y)MO_3$, worin A zumindest ein Erdalkalimetall ist, M Mangan oder Kobalt ist und y $0 \leq y \leq 0,4$, einen Zirkoniumoxid-Festelektrolytfilm (2), der Mangan oder Kobalt enthält, das zumindest in der Nähe der Grenzfläche zum Luftelektrodensubstrat als feste Lösung vorliegt, und

FIG. 3